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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

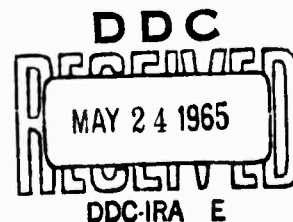
FOURTEENTH QUARTERLY TECHNICAL SUMMARY REPORT
1 January - 31 March, 1965

Contract No. Nonr-3593(00)
ARPA Order No. 23-63, Amendment No. 38
Program Code No. 4910

MRI Project No. 2551-P

For

Director
Advanced Research Projects Agency
Washington, D. C.



425 VOLKER BOULEVARD/KANSAS CITY, MISSOURI 64110/AC 816 LO 1-0202

MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

by

Thomas A. Milne
Frank T. Greene

FOURTEENTH QUARTERLY TECHNICAL SUMMARY REPORT
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MIDWEST RESEARCH INSTITUTE

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PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00), monitored by Mr. Roland Jackel and Dr. Ralph Roberts of the Power Branch, ONR.

The report describes additional studies on sulfur, boron and iron species in flames. Velocities of beam components were measured by a time-of-flight method and nucleation of argon and water was studied.

The research staff consists of Dr. Thomas A. Milne, project leader, Dr. Frank T. Greene and Mr. Jacob Beachey. It is a pleasure to acknowledge the active interest and participation of Mr. Gordon Gross in this research.

Approved for:

MIDWEST RESEARCH INSTITUTE



Sheldon L. Levy, Director
Mathematics and Physics Division

19 May 1965

TABLE OF CONTENTS

	<u>Page No.</u>
Summary	1
I. Introduction	2
II. Species in One Atmosphere Flames	2
III. Velocity Measurements of Supersonic Molecular Beams	4
IV. Further Nucleation Studies	10
V. Future Work	13
References	14

SUMMARY

Sampling results on sulfur, boron and iron species in flames are reported. Aerodynamic molecular beam velocities were measured by a simple phase-shift method for Ar-He and Ar-N₂ mixtures. Nucleation phenomena in such beams are reported for wet and dry argon and for Ar-Kr mixtures. The effect of pressure and orifice size on argon dimer concentration is given. Evidence exists of substantial knock-on effects involving the large water background present in the sampling system.

I. INTRODUCTION

A summary of our sampling tests on free radicals and noncondensable species has been written for publication^{1/} and will be distributed as a topical report. Some anomalies with sulfur species have been resolved and a few experiments with BCl_3 and $\text{Fe}(\text{CO})_5$ in $\text{H}_2\text{-O}_2$ flames have also been carried out.

During the past quarterly period we interrupted our attack on the problems of sampling highly condensable species to obtain some data of more general interest to high pressure sampling. The studies consisted of time-of-flight beam velocity analyses and further studies on nucleation. This effort was partly motivated by the occurrence of a small informal conference on direct, high-pressure sampling held May 6 and 7 at Midwest Research Institute. Abstracts of the papers presented and a list of attendees will be available in June to interested persons.

II. SPECIES IN ONE ATMOSPHERE FLAMES

The studies of sulfur containing species in rich and lean $\text{H}_2\text{-O}_2$ flames were repeated more carefully and the anomalies mentioned in the Thirteenth Quarterly^{2/} were not observed. When a few per cent of either H_2S or SO_2 was added to a rich 5-1 $\text{H}_2\text{-O}_2$ flame, virtually identical species profiles were obtained, as shown in Fig. 1. Note the very high, initial concentrations of SO , S and SO_2 and the late appearance of SH and SH_2 . Further study of this system would provide a useful test of quenching in a complex case where a number of species of well known thermodynamics are involved. Also new insight into the mechanism of combustion of sulfur compounds might be obtained. We have deferred further studies on this system, however, in favor of work with highly condensable species.

In a lean 2-4 $\text{H}_2\text{-O}_2$ flame with either SO_2 or H_2S added, the $\text{SO}_2^+/\text{SO}^+$ ratio was nearly constant through the flame and only slightly lower than for cold, pure SO_2 . This agrees with equilibrium calculations that show that SO_2 is the major species. It may be that with more careful study of appearance potentials and fragmentation patterns, one can shed light on the postulated existence of an isomer of SO_2 ,^{3/} with a peroxide bonding, believed to be formed in the early stages of the combustion of sulfur compounds.

Several more attempts were made to see Fe or FeO in a CO-O_2 flame to which $\text{Fe}(\text{CO})_5$ had been added. During one run, there seemed to be a clear increase in the 72^+ peak (FeO^+) upon adding $\text{Fe}(\text{CO})_5$ to the flame. However, subsequent tests were negative. It is apparent that simpler, better known metal systems must be used to unravel the difficulties in such sampling.

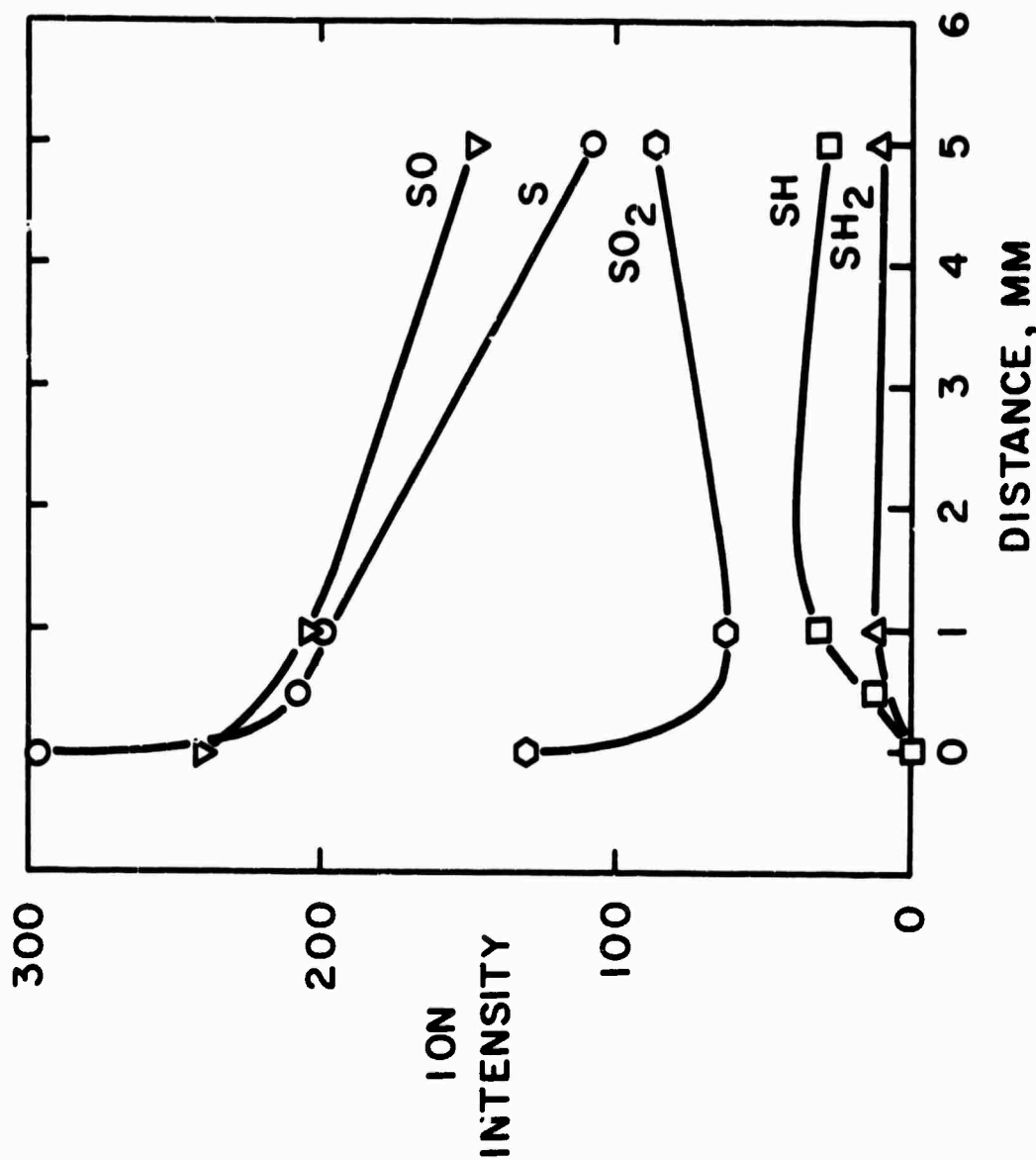


Fig. 1 - Sulfur Containing Species Observed in a Rich 5-1 H_2-O_2 Flame When Either H_2S or SO_2 Are Added. Distance is measured from the point at which the conical probe just touched the visible reaction zone.

The previously reported observation of O, HCl and H₂O₂, when BCl₃ is added to a H₂-O₂ flame, was confirmed by adding 0.1 per cent BCl₃ to a lean 2-4 H₂-O₂ flame. The H₂O₂⁺ species was observed with an intensity which was within a factor of two of that predicted, thus indicating quantitative sampling. However, several disturbing features were noted. In such systems, condensate does not form initially on the hottest portion of the sampling orifice. A deposit of oxide-hydroxide does build up on the cooler portion of the orifice and gradually encroaches on the region in front of the orifice. After an hour or more, the orifice may become completely covered with a porous sphere of oxide. Often a substantial molecular oxygen beam will still be present in this partially plugged condition even though there remains no line of sight path into the mass spectrometer. Furthermore, after many hours of sampling, a thick, loose deposit has been observed to build up on the inside of the sampling orifice cone, threatening to interrupt line of sight access even if the exterior of the cone is periodically cleaned.

One obvious approach to the alleviation of these problems is to work with smaller concentrations of metal. We had not yet availed ourselves of the reported advantages of the "Studier"⁴ mode of operation of the Bendix. Consequently this mode was activated in our instrument by minor changes and an immediate gain in beam-ion intensity of a factor of 20 was obtained, with no adjustment of ion source magnets. It is hoped that further gains can be achieved, thus allowing us to use smaller quantities of metal additives for a given signal-to-noise ratio.

III. VELOCITY MEASUREMENTS OF SUPERSONIC MOLECULAR BEAMS

A mass spectrometer with an electron bombardment ion source measures molecular densities. Consequently, when used as a molecular beam detector a mass spectrometer gives a total signal which is dependent on the velocity distribution as well as on the flux of the species being studied. If the beam is formed from an effusive source, the effect of flux and velocity will cancel.⁵ In a supersonic molecular beam, however, the concentration of a particular species in the beam is not directly related to its ultimate velocity distribution, and an assumption about the velocity distributions of various species is required. In the past work on this project we have assumed that all species in the beam have the same velocity distribution. This assumption could result in an appreciable error for species with large differences in mass. Consequently, we desired to measure component velocities directly in our sampling system.

The "lock-in" amplifiers, which have been incorporated into the modulated beam system, provide a simple means of measuring the most probable velocity of a beam component by the time-of-flight method. The apparatus used

is shown schematically in Fig. 2. The beam chopper consists of a disk, containing 18 radial slots, which is mounted on a synchronous motor operating at 3,600 rpm. The beam was chopped immediately in front of the skimmer. The orifice-to-skimmer distance was kept very large to insure that the chopper wheel was in a molecular flow region. The reference signal was generated by a light beam which was interrupted by the opposite side of the chopper wheel before being detected by a photodiode. The reference signal from the photodiode and the mass spectrometer signal were introduced into Princeton Applied Research Models JB4 and JB5 lock-in amplifiers. Within these units the reference and mass spectrometer signals were amplified by narrow band amplifiers, the reference signal was then passed through a variable phase shifter and both signals were introduced into a phase sensitive detector. The output of the phase sensitive detector was then amplified and integrated. The output of the PAR amplifiers was read from strip chart recorders. The shift of the reference signal phase was measured by a AD-YU Type 405H Precision Phase meter.

The intensity of a particular beam component was plotted against phase shift, and the maximum in the curve determined by the method of rectangular diameters. At this maximum, the signals produced by the reference and the mass spectrometer are in phase. Since the angle between the light and molecular beams was not sufficiently well known to allow the absolute phase shift to be determined from first principles, it was necessary to calibrate the system against a 1 atm. argon beam under the assumption that the argon beam had reached its maximum velocity (the velocity as $M \rightarrow \infty$).

The most probable velocity of argon beams formed from several different source pressures are given in Fig. 3, from which it can be inferred that an argon beam formed from 1 atm. with a 0.002 in. orifice has very nearly reached its limiting velocity. This result is consistent with the expression of Fenn,⁶ which predicts a terminal Mach number of 10-12 under these conditions. All subsequent measurements were then made with respect to a 1 atm. argon beam.

The measured velocities for the components of several He-Ar and N₂-Ar beams are given in Figs. 4 and 5. The solid line gives the maximum stream velocities calculated as a function of gas composition. The observed velocities are believed to be accurate to ± 3 per cent; velocity differences for a particular mixture should be considerably more accurate. These results are not corrected for the small effect the velocity distribution has in shifting the observed maximum velocity from the true beam maximum velocity.

For the Ar-N₂ mixtures the velocity differences between the two components is small over the entire composition range, and can be neglected for most sampling applications. In the helium rich He-Ar mixtures, on the other hand, the argon lags the He by about 7 per cent, which would cause an appreciable error in some applications although not in our flame work.

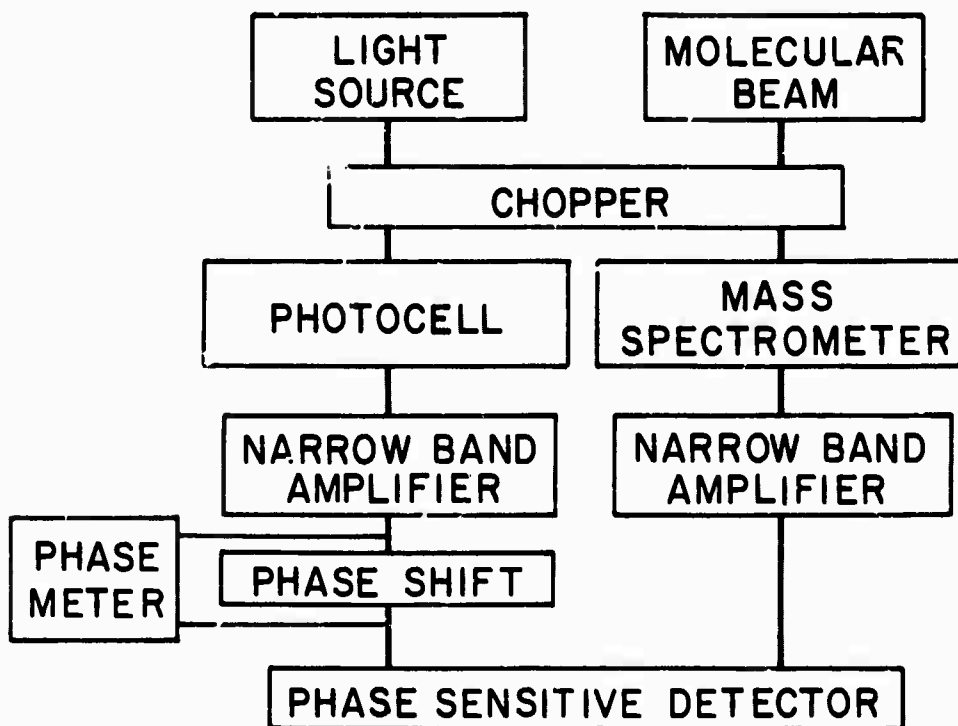


Fig. 2 - Molecular Beam Time-of-Flight Apparatus

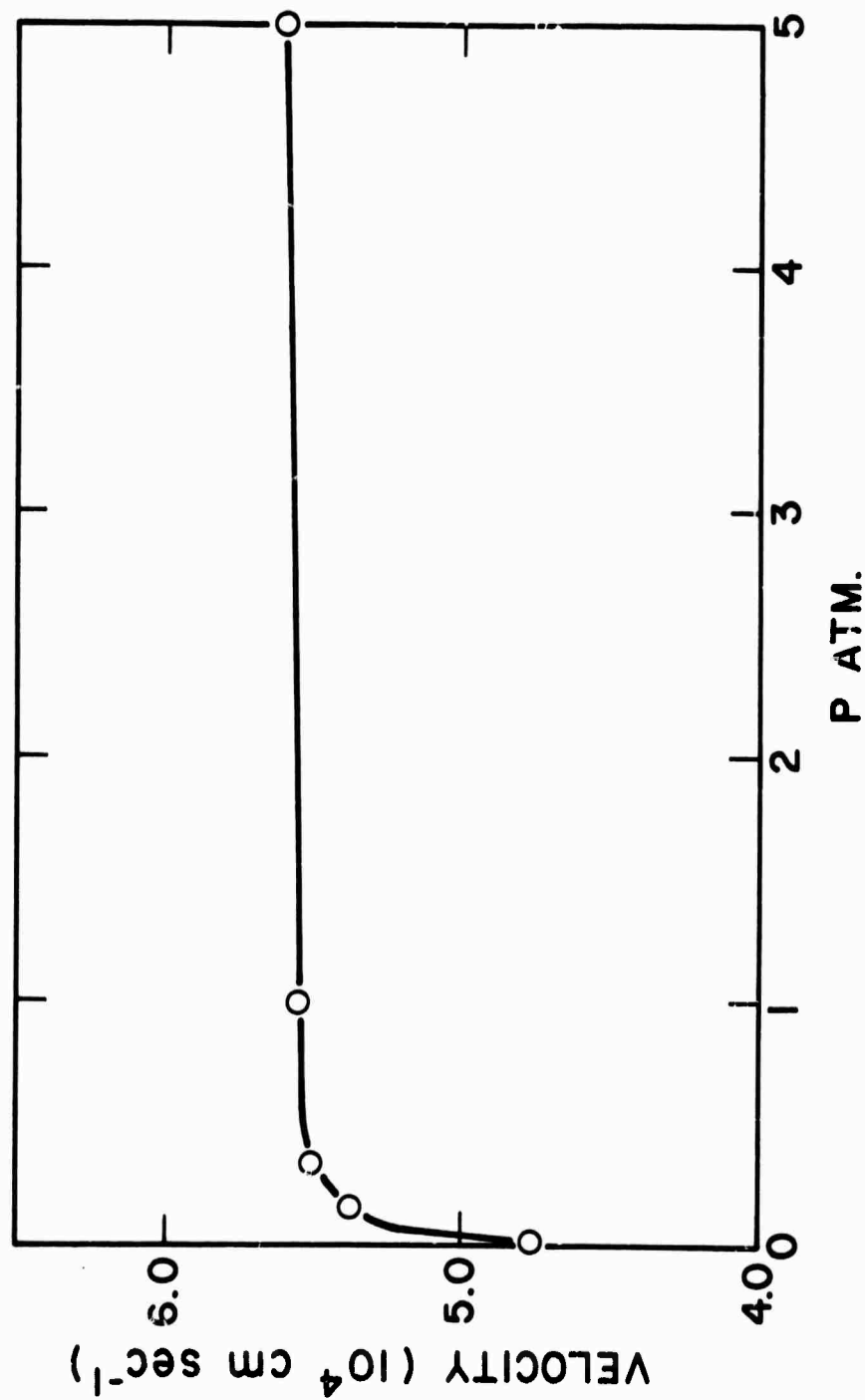


FIG. 3 - Measured Velocities of Argon Beams as a Function of Pressure. A 0.002 in. orifice was used.

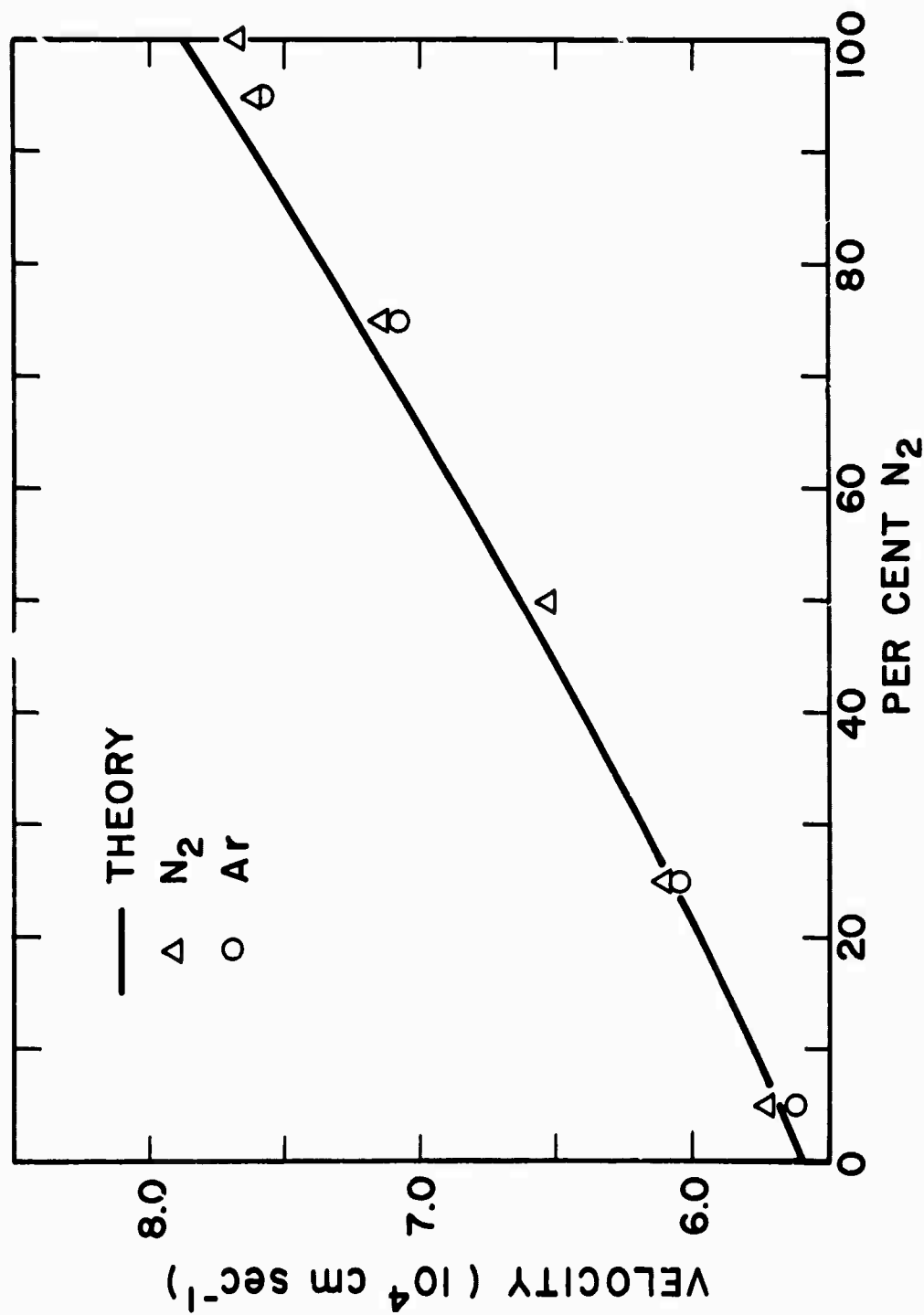


Fig. 4 - Measured Velocities in N₂-Ar Supersonic Beams. The theoretical line gives the maximum velocity calculated for the mixture. A 0.002 in. orifice and 1 atm. total source pressure were used.

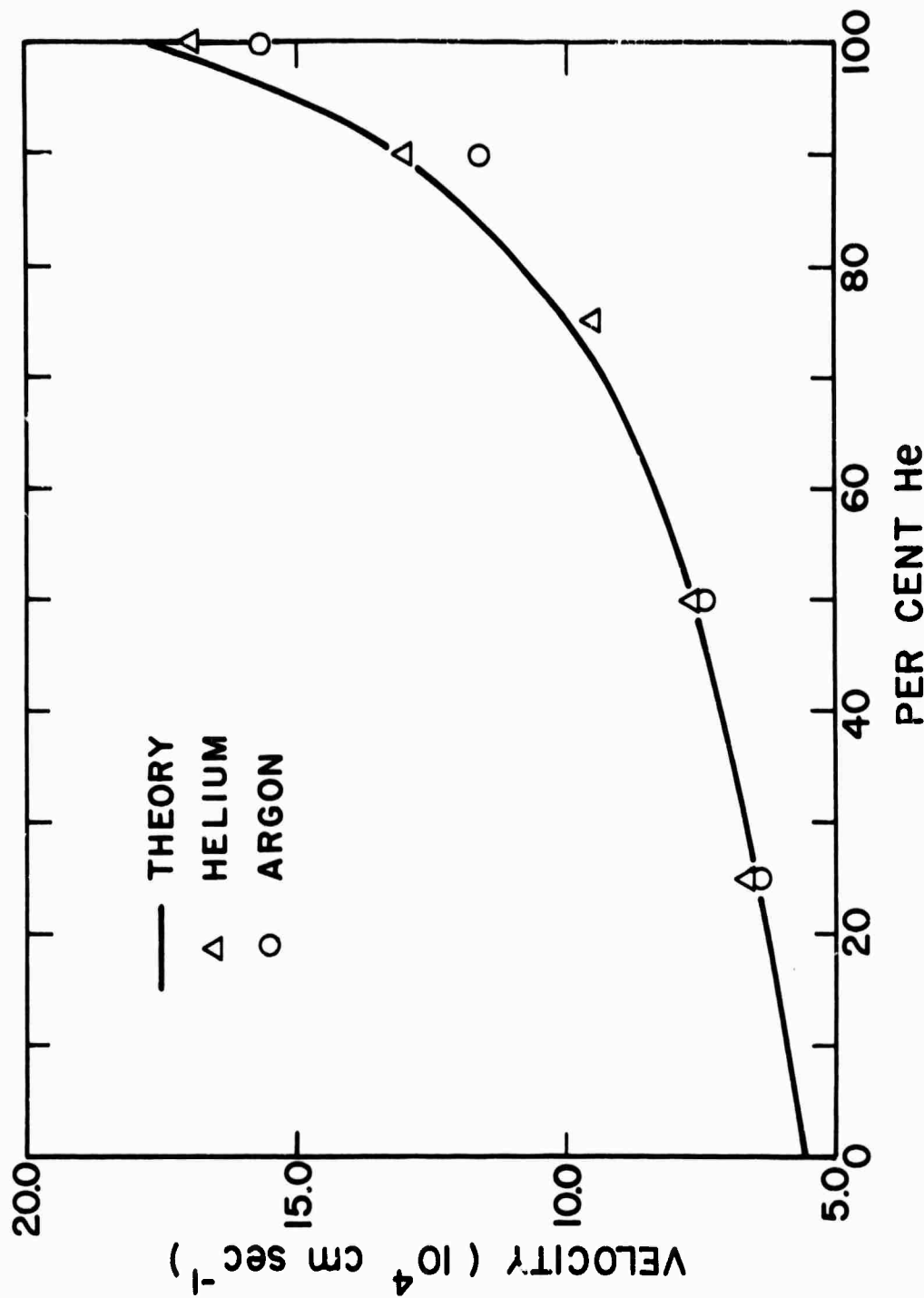


Fig. 5 - Measured Velocities in He-Ar Supersonic Beams. The theoretical line gives the maximum velocity calculated for the mixture. A 0.002 in. orifice and 1 atm. total source pressure were used.

IV. FURTHER NUCLEATION STUDIES

The nucleation phenomena observed in high pressure beam formation, and reported earlier^{7,8} may present serious limitations in sampling. One of the least ambiguous ways of distinguishing equilibrium species from those formed by nucleation during expansion may be the observations of cluster concentration versus pressure and orifice size. During the past quarter we tested this dependence at several pressures for orifices ranging from 0.0005 in. to 0.012 in. diameter.

A great deal of data was gathered on cluster concentration in pure argon. Scattering experiments in each stage were carried out to observe the effect on cluster distribution. The approximate pressure dependence of cluster concentration is shown in Fig. 6 for a 0.004 in. diameter orifice. One feature worth pointing out and which typifies the wealth of information which such studies may eventually give on the kinetics and free energies of clusters is the anomalously low value of the Ar_{20}^+ peak (mass 800). The other features of the 5-atm. distribution may be statistical in nature but the dip of 800^+ between 760^+ and 840^+ was established repeatedly. Is this a property of the 300^+ ion? The free energy of the Ar_{20} neutral? Or kinetics?

When orifice size is increased over a certain range at sufficiently high pressure, the T-P history of the expansion is simply lengthened with virtually the same final state achieved. The resulting effect on monomer-to-dimer ratio, at several pressures, is shown in Fig. 7. The value of $40^+/80^+$ at zero orifice size should be close to the equilibrium value, and indeed, agrees quite well with Hirschfelder's⁹ calculations of equilibrium dimer concentration from second virial coefficients. This data and much more which is not presented here will be analyzed for its kinetic, thermodynamic and sampling implications.

Clusters containing more than one kind of species were observed on several occasions. In some early experiments with 5 atm. argon a wet rubber hose was used to introduce the argon. Under this circumstance an extensive series of pure water clusters were observed. Several mixed clusters were also seen although greatly reduced in concentration, as shown in Table I. In later runs with a dry rubber hose inlet, another series of species were readily discernible. These species consisted of clusters of argon atoms containing one H_2O each, $(\text{Ar}_x \cdot \text{H}_2\text{O})^+$. An Ar-Kr mixture at 5 atm. gave comparable quantities of Ar_2^+ , ArKr^+ and Kr_2^+ . This result would be expected on either kinetic or equilibrium grounds.

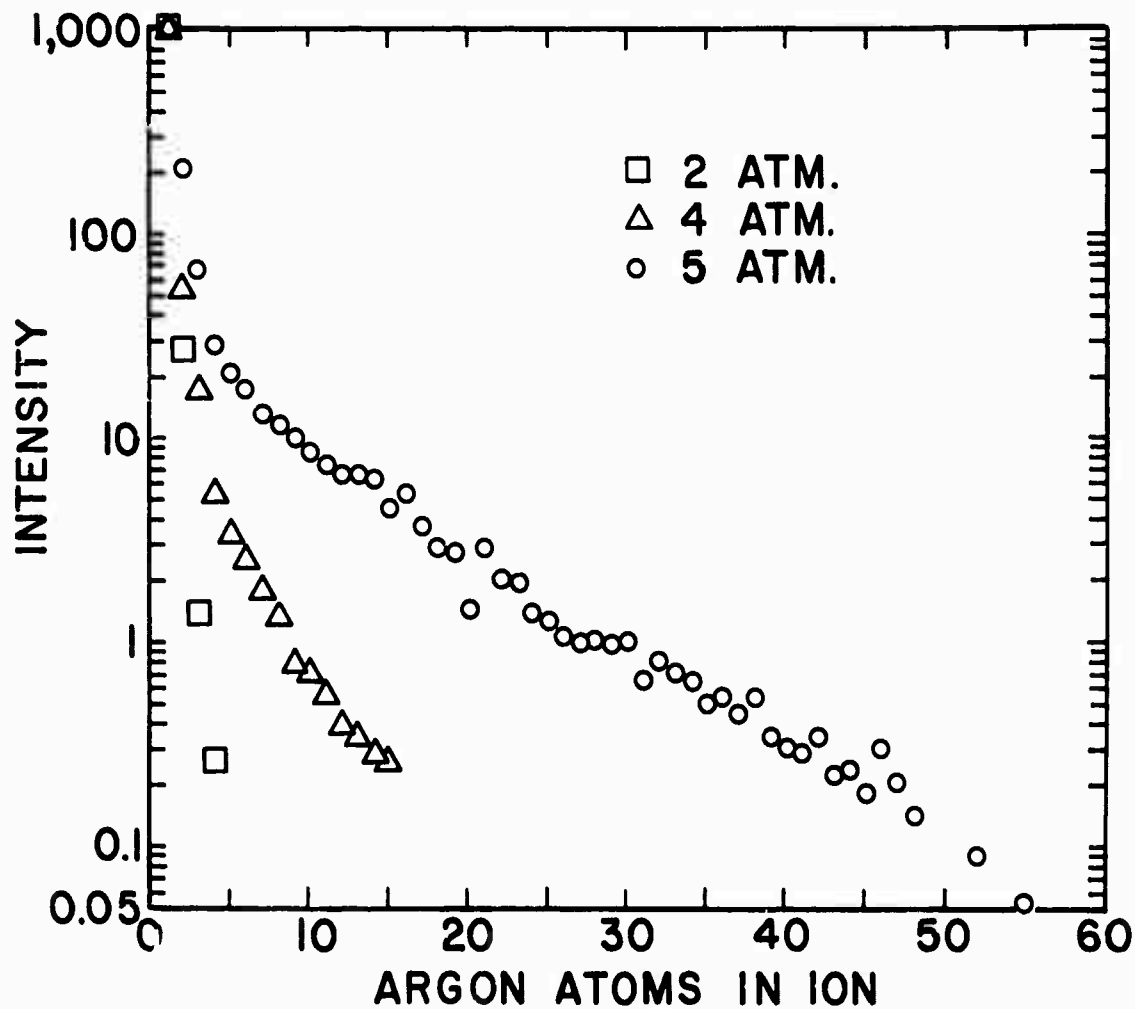


Fig. 6 - Cluster Distribution in Argon at Several Pressures,
Sampled Through a 0.004 In. Diameter Orifice

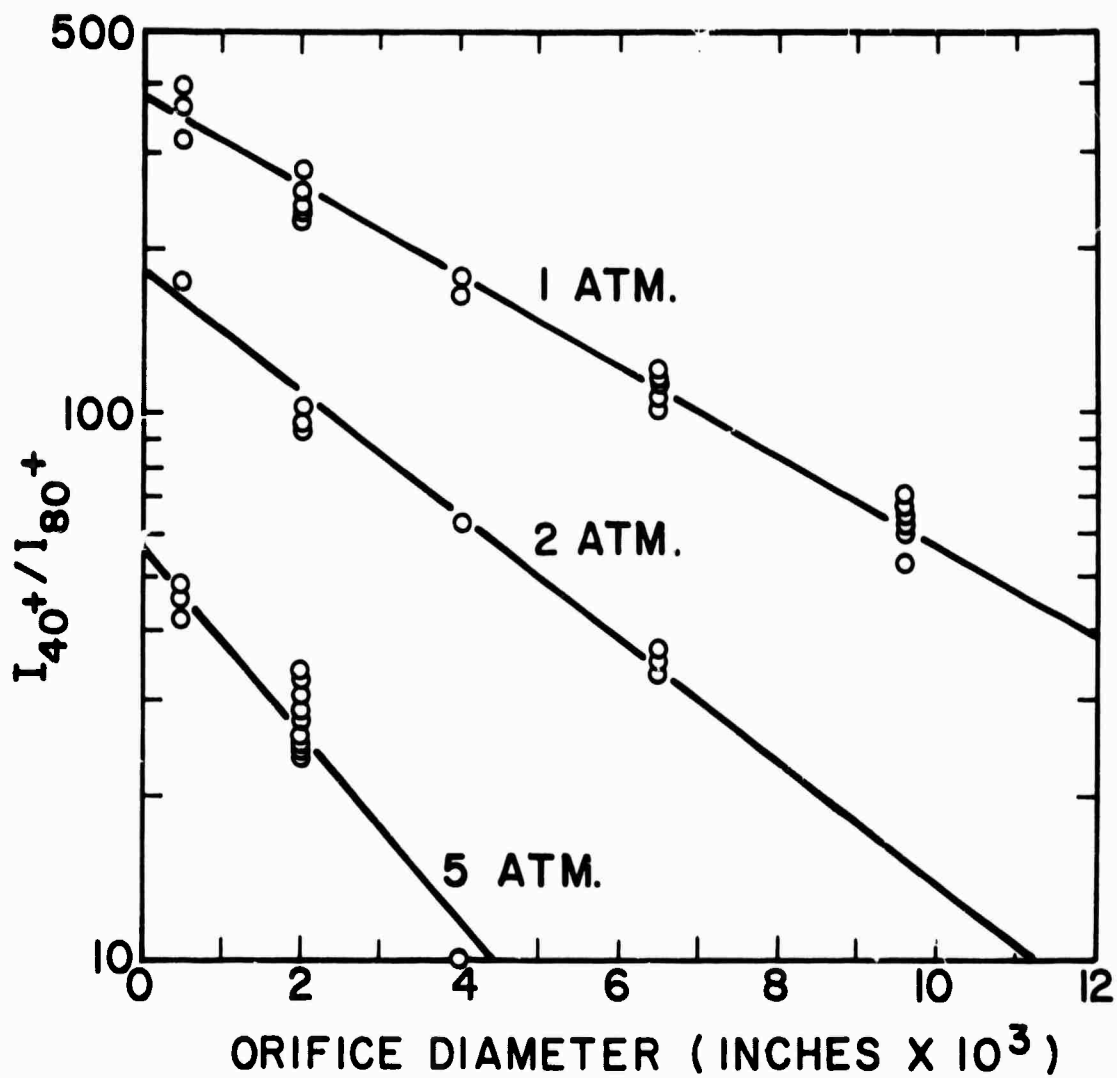


Fig. 7 - Effect of Orifice Size on Argon Dimer Concentration
at Several Source Pressures of Pure Argon

TABLE I

CLUSTERS OBSERVED IN SAMPLING WET ARGON AT 5 ATM.
THROUGH A 0.002 IN. DIAMETER ORIFICE

<u>x</u>	<u>(Ar)_x</u>	<u>(H₂O)_x</u>	<u>H₂O·(Ar)_{x-1}</u>	<u>Ar·(H₂O)_{x-1}</u>
1	100	0.40	0.40	100
2	4.1	0.63	0.15	0.15
3	0.81	0.81	0.042	0.049
4	0.27	0.52	0.016	
5	0.14	0.31		

In the course of this work a fairly definite knock-on effect was seen with background water. Very dry tank argon was introduced through dry copper lines at 1 - 5 atm. A substantial water beam was seen as well as a 19⁺ beam peak due to water dimer. These peaks both became much less at 1 atm. relative to Ar, indicating a knock-on phenomena similar to that seen by Nutt.^{10/} It also appears that the knock-on water can nucleate in subsequent collisions. Further details of the nucleation work plus an interpretation of some of the observations will be the subject of a forthcoming paper.

V. FUTURE WORK

Once again our attention turns fully to the problem of sampling highly condensable species in flames so that we can get onto a number of interesting thermodynamic studies. The line of attack will be to try to determine the relative importance of flame-probe interaction versus nucleation in limiting the sampling of condensable species. Further improvements in signal/noise ratio with the "Studier" mode will be sought first. The elements B, Fe, Si and Ti will be introduced into flames of appropriate temperature and environment for test purposes.

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